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(54) Energy beam curable epoxy resin composition, stereolithographic resin composition and stereolithographic method

(57) The energy beam curable epoxy resin composition comprising as essential components, (1) specific cationically polymerizing organic substance, (2) energy beam sensitive cation polymerization initiator, (3) cationically polymerizing organic substance except for the specific cationically polymerizing organic substance, described above, (4) radically polymerizing organic

compound, and (5) energy beam sensitive radical polymerization initiator. The cured articles resulted from said resin composition, have superior properties and particularly superior dimensional stability on humidity absorption. Therefore, a stereolithographic resin composition and a stereolithographic method are also provided.

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DescriptionBackground of the Invention

5 [Field of the Invention]

The present invention relates to an energy beam curable epoxy resin composition which is curable upon exposure to an energy beam such as an ultraviolet ray or an electron beam, a stereolithographic resin composition using said resin composition and a stereolithographic method. More specifically, the present invention relates to an energy beam curable epoxy resin composition to give the cured resin, which has chemical resistance, water-resistance, humidity-resistance, good adhesive property and reduced shrinkage on curing, a stereolithographic resin composition using said resin composition and a stereolithographic method.

15 [Related ART]

Recently, resin compositions, which are curable upon exposure to an active energy beam such as an ultraviolet ray or an electron beam, are used in various applications such as paint and varnish, coatings, adhesives, sealing compounds and the like. A photo-curable epoxy resin composition is known as one of said energy beam curable resin compositions as described in, for example, Japanese Patent Application No. SHO 63-113022, No. HEI 3-77210, Japanese Patent Application Laid-open No. HEI 1-149848, No. HEI 2-114022, No. HEI 4-266,985.

20 The photo-curable epoxy resin composition is not influenced with oxygen on curing, being unlike a radically polymerizing photo-curable resin, has superior physical properties such as an adhesive property in the cured articles, and then is expected to be used in wide applications.

25 This photo-curable epoxy resin composition is composed essentially of an epoxy resin and a photopolymerization initiator. Onium salts are known to be used as a photopolymerization initiator.

30 Alicyclic epoxy ester compounds, which typically include 3,4-epoxy cyclo-methyl-3,4-epoxy cyclohexane carboxylate "Cylacure UVR-6110, Union Carbide Corp., or Ceroxide-2021, Dacel Chemical Industries LTD." and bis (3,4-epoxy cyclohexylmethyl) adipate "Cylacure UVR-6128, Union Carbide Corp.", are used as a main component for a photopolymerization initiator-curable epoxy resin, since they have preferable reaction rate and physical properties.

35 A stereolithographic method is a technique, as described in Japanese Patent Application Laid-open No. SHO 60-247515, wherein a given portion of photo-curing resin placed in a vessel is exposed continuously to a beam such as argon, helium-cadmium or semiconductor laser from above to cure the exposed portion, in order to produce a desired plane of cured layer. Then the cured layer is overlaid with another layer of the photo-curing resin, which is then photo-cured in the same manner to produce a second cured layer which continuously overlaps the first layer; and the same process is repeated to finally obtain a desired three-dimensional solid shape.

40 As resins previously used for the above-described stereolithographic method, mention may be made of radically polymerizing resin compositions and, for example, Japanese Patent Application Laid - open No. HEI 2-228312 and No. HEI 5-279436 disclose a stereolithographic resin composition composed mainly of (meth)acrylic resin. Further, Japanese Patent Application Laid-open No. HEI 2-145616, with the aim of reducing deformation, discloses a stereolithographic resin which contains liquid resin and fine particles whose difference in apparent specific gravity is less than 0.2. For producing moldings at higher precision, Japanese Patent Applications Laid-open No. HEI 3-15520 discloses a composition comprising an unsaturated ethylene-derivative monomer, a photo-initiator, and a potentially insoluble, potentially radioactive polarizing substance, and Japanese Patent Applications Laid-open No. HEI 3-41126 discloses a composition comprising an unsaturated ethylene-derivative monomer, a photo-initiator, and a potentially soluble radio-polarizing substance, respectively. In addition, Japanese Patent Application Laid-open No. HEI 4-85314 discloses a resin composition comprising a silicone urethane acrylate, a compound having multifunctional ethylene-type unsaturated bonds, and a polymerization initiator.

45 Another stereolithographic resins are known cationically polymerizing resin composition. For example, Japanese Patent Application Laid-open No. HEI 1-213304 discloses a cationically polymerizing resin composition characterized by comprising a cationically polymerizing energy beam curable organic compound and a energy beam sensitive cationic polymerization initiator. Japanese Patent Application Laid-open No. HEI 2-28261 discloses a resin comprising a cationically polymerizing energy beam curable organic compound and a portion of a radically polymerizing radio-curing organic compound, which exhibits reduced shrinkage and improved resolution. Also, Japanese Patent Application Laid-open No. HEI 2-80423 discloses a resin composition comprising an epoxy resin, a vinyl ether resin, an energy beam sensitive cationic polymerization initiator, a radically curing resin, and an energy beam sensitive radical polymerization initiator. In addition, Japanese Patent Application Laid-open No. HEI 2-75618 discloses a stereolithographic resin composition characterized by comprising a cationically polymerizing energy beam curable organic compound, an energy beam sensitive cationic polymerization initiator, a radically polymerizing energy beam curable organic com-

5 pound, an energy beam sensitive radical polymerization initiator, and a polyester having hydroxyl groups.

6 Among the conventional stereolithographic resin compositions as described above, photo-curable epoxy resin compositions composed mainly of an alicyclic epoxy ester compound generally have improved brightness, heat resistance, chemical resistance and reduced shrinkage on curing in cured articles and thus are used for paint and varnish, 10 coatings, adhesives, sealing compounds and the like. However, the cured articles are required to improve some properties such as alkali-resistance, water-resistance and adhesive property and also express the change in dimensions due to moisture absorption.

15 Further, any of a radically polymerizing resin and a stereolithographic resin composition composed mainly of it is prevented from curing under oxygen, which results in low degree of cure on curing, so that it is necessary to carried out "post cure process" by ray or heat, which is necessarily concerned in curing of mold. In the post cure process, however, the moldings has such a disadvantage as being apt to deform. Further, these resins show large shrinkage on curing, which makes it difficult to obtain a molding with desirable dimension.

15 Furthermore, cationically curable stereolithographic resins as described in Japanese Patent Application Laid-open No. HEI 1-213304, No. HEI 2-28261 and No. HEI 2-75618, have such superior characteristic properties that the post cure process are not necessary and the deformation are little, as the curing proceeds through an active group even, after the beam to be exposed are shut down, and it is also easy to obtain a molding with desirable dimension because of small shrinkage on curing. However, these resins have such disadvantages that they have insufficient sensitivity to an energy beam to be exposed, and the cured articles show the deformation by humidity-absorption because of its humidity-absorption.

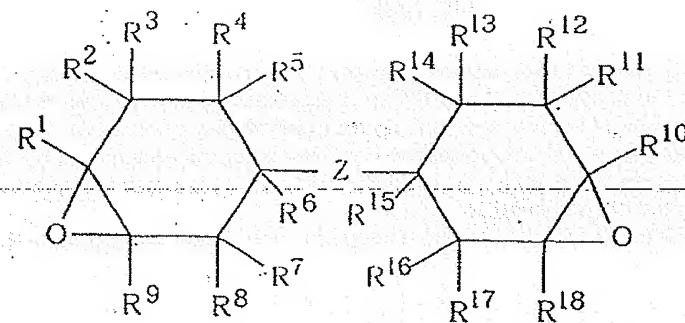
20 On the other hand, Japanese Patent Application Laid-open No. SHO 58-172387 discloses a method of producing 2,2-dicyclohexenylpropane di-epoxide, and Japanese Patent Application Laid-open No. SHO 48-29899 discloses an epoxy resin composition consisting of methylene bis(3,4-epoxy cyclohexane) and polycarbonic acid anhydride, which can be cured by heating. However, it has never been known hitherto, whether these alicyclic epoxy compounds are suitable for photo-curing or lithographic molding, or not.

25 Therefore, the object of the present invention is to provide an energy beam curable epoxy resin composition, a stereolithographic resin composition and a stereolithographic method, which can give the improved cured article, having superior physical properties and a high dimensional stability under humidity absorption.

Summary of the Invention

30 In order to attain the object described above, an energy beam curing epoxy resin composition of the present invention comprises as essential components thereof:

35 (1) a cationically polymerizing organic substance, having the general formula as follows,



40 where 'Z' is a radical, having a valence of 2, selected from the group consisting of oxygen, sulfur, -NH-, -SO-, -SO₂-, -CH₂-, -C(CH₃)₂-, -CBr₂-, -C(CBr₃)₂-, and -C(CF₃)₂-, and R¹~R¹⁸, which may be identical or non-identical to each other, are hydrogen, halogen, hydrocarbon group, which may contain oxygen or halogen, or alkoxy group, which may be substituted; and

45 (2) an energy-beam sensitive cationic polymerization initiator.

The energy beam curable epoxy resin composition of the present invention may further comprise,

(3) a cationically polymerizing organic substance except for that of the aforementioned general formula (I).

The energy beam curable epoxy resin composition of the present invention may furthermore comprise,

(4) a radically polymerizing organic compounds; and

(5) an energy beam sensitive radical polymerization initiator.

In the energy beam curable epoxy resin composition, it is preferable that 50 wt% or more of (4) radically polymerizing organic compound is a compound having (meth)acrylic group per one molecule.

5 Further, a stereolithographic resin composition of the present invention comprises using the energy beam curable resin composition described above.

10 Furthermore, a stereolithographic method of the present invention, wherein a given portion of an energy beam curing resin composition is exposed to an energy beam to cure the exposed portion thereof, in order to produce a desired thickness of cured layer; then, the cured layer is overlaid with another layer of the energy beam curable resin composition, which is then cured in the same manner to produce a second cured layer which continuously overlaps the first layer; and the same process is repeated to finally obtain a three-dimensional molding; comprises using the stereolithographic resin compositions of the present invention described above as an energy beam curable resin composition.

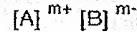
15 Description of the Preferred Embodiments

According to the present invention, in (1) cationically polymerizing organic substance having the general formula (I) described above, 'Z' in the formula (I) is a radical, having a valence of 2, selected from the group consisting of oxygen, sulfur, -NH-, -SO-, -SO₂-, -CH₂-, -C(CH₃)₂-, -CBr₂-, -C(CBr₃)₂- and -C(CF₃)₂-, preferably -SO₂-, -CH₂-, -C(CH₃)₂-, or -C(CF₃)₂-, particularly preferably -CH₂- or -C(CH₃)₂-. R¹~R¹⁸ in the formula (I) may be identical or non-identical to each other, and are hydrogen, halogen, hydrocarbon group, which may contain oxygen or halogen, or alkoxy group, which may be substituted, and preferably may be identical or non-identical to each other, and are hydrogen, chlorine, methyl group, ethyl group or methoxy group, particularly preferably hydrogen.

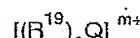
25 In the present invention, two or more cationically polymerizing organic substances having the general formula (I) described above can be used in combination.

20 (2) Energy beam sensitive cationic polymerization initiator, which is used according to the present invention, is a compound which can emit a substance that initiates cationic polymerization upon exposure to an energy beam, preferably a double salt of an onium which emits a Lewis acid upon exposure, or a derivative thereof. A typical example of such compounds is a salt of a cation and an anion, expressed generically by a following formula:

30



35 Preferably, the cation A^{m+} is an onium having a structure such as one expressed as the following general formula:



40 Here, R¹⁹ is an organic group having 1 to 60 carbons and any number of non-carbon atoms. The number 'a' is an integral number in the range of 1 to 5. The 'a' groups, R¹⁹, are independent of and may be identical or non-identical to each other; preferably, at least one of them is to be an organic group having an aromatic ring as described above. The symbol 'Q' denotes an atom or an atomic group selected from the group consisting of S, N, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, F and N=N. Assuming the valence of 'Q' in the cation A^{m+} as 'q', it is required that the relation m = a - q is observed, (here, the valency of 'N=N' is assumed as O).

45 The anion B^{m-} is preferably a halide complex having a structure such as one expressed as the following general formula:



50

Here, 'L' is a central metal or metalloid atom of the halide complex, such as B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn or Co. The symbol 'X' denotes a halogen. The number 'b' is an integral number in the range of 3 to 7. Assuming the valence of 'L' in the anion B^{m-} as 'p', it is required that the relation m = b - p is observed.

55 Examples of anions expressed by the above generic formula [LX_b]^{m-} include tetrafluoroborate (BF₄)⁻, hexafluorophosphate (PF₆)⁻, hexafluoroantimonate (SbF₆)⁻, hexafluoroarsenate (AsF₆)⁻, and hexachloroantimonate (SbCl₆)⁻.

A structure expressed as [LX_{b-1}(OH)]^{m-} may also preferably be used as the anion B^{m-}, where 'L', 'X' and 'b' are defined as described above. Other suitable anions include perchloric ion (ClO₄)⁻, trifluoromethylsulfurous ion (CF₃SO₃)⁻, fluorosulfonic ion (FSO₃)⁻, toluenesulfonic anion, and trinitrobenzenesulfonic anion.

In the present invention among these onium salts mentioned above, it is particularly effective to use aromatic onium salts of (a) to (c) as follows. One or more kinds of these onium salts can be used as a mixture thereof.

- (a) Aryl diazonium salts such as phenyl diazonium-hexafluorophosphate, 4-methoxyphenyl diazonium-hexafluorophosphate and 4-methylphenyl diazonium-hexafluorophosphate,
- (b) diaryliodonium salts such as diphenyl iodonium-hexafluoroantimonate, di(4-methylphenyl) iodonium-hexafluorophosphate and di(4-tert-butylphenyl) iodonium-hexafluorophosphate,
- (c) triaryl sulfonium salts such as triphenyl sulfonium-hexafluoroantimonate, tris(4-methoxyphenyl) sulfonium-hexafluorophosphate, diphenyl-4-thiophenoxyphenyl sulfonium-hexafluoroantimonate, diphenyl-4-thiophenoxyphenyl sulfonium-hexafluorophosphate, 4,4'-bis(diphenylsulfonio)phenylsulfid-bis-hexafluoroantimonate, 4,4'-bis(diphenylsulfonio)phenylsulfid-bis-hexafluoroantimonate, 4,4'-bis[di(β-hydroxyethoxy)phenylsulfonio] phenylsulfid-bis-hexafluorophosphate, 4[4'- (benzoyl)phenylthio] phenyl-dl-(4-fluorophenyl)sulfoniumhexafluoroantimonate and 4 [4'- (benzoyl)phenylthio]phenyl-di-(4-fluorophenyl)sulfoniumhexafluorophosphate.

Further, mention may be made of iron-arene complex such as $(\eta^5\text{-}2,4\text{-cyclopentadiene-1-yl})[(1,2,3,4,5,6,\text{-}\eta)\text{-}(1\text{-methylethyl)benzene}]$ -iron-hexafluorophosphate, and the mixture of aluminium complex such as tris (acetylacetato)aluminium, tris(ethylacetatoacetate)aluminium, tris(salicylaldehyde)aluminium, with silanol such as triphenyl silanol.

Among these compounds, aromatic iodonium salts, aromatic sulfonium salts and iron-allene complex are preferably used from viewpoint of practical use and photo-sensitivity.

(3)Cationically polymerizing organic substance except for that having the aforementioned general formula (I), which is used in the present invention is a compound which polymerizes or cross-links in the presence of an energy beam sensitive cationic polymerization initiator which is activated by exposure to an energy beam, except for the cationically polymerizing organic substance having the above mentioned general formula (I).

Examples of such compounds include epoxy compounds, cyclic ether compounds, cyclic lactone compounds, cyclic acetal compounds, cyclic thioether compounds, spiroorthoester compounds, and vinyl compounds, which have the structure except for the cationically polymerizing organic substance having the general formula (I) described above. They may be used independently or in combination. Among them, epoxy compounds are suited, for their availability and ease of handling. As such epoxy compounds, aromatic, alicyclic, aliphatic epoxy resins, and the like are mentioned.

Examples of the aromatic epoxy resins described above, include polyglycidyl ethers of polyhydric phenols having at least one aromatic ring, or their adducts with alkylene oxide, such as bisphenol A, bisphenol F, the glycidyl ethers of their adducts with alkylene oxides, or epoxy-novolac resins.

Further, examples of the alicyclic epoxy resins described above, include polyglycidyl ethers of poly-hydric alcohols having at least one alicyclic ring, or a compound containing cyclohexane-oxide or cyclopentene-oxide obtained by epoxidation of a compound having a structure of cyclohexene- or cyclopentene-ring with oxidant. For example, mention may be made of diglycidyl ether of hydrogenated bisphenol A, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-1-methylcyclohexyl-3,4-epoxy-1-methylcyclohexane carboxylate, 6-methyl-3,4-epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-3-methylcyclohexylmethyl-3,4-epoxy-3-methylcyclohexane carboxylate, 3,4-epoxy-5-methylcyclohexylmethyl-3,4-epoxy-5-methylcyclohexane carboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-methadioxane, bis(3,4-epoxycyclohexylmethyl) adipate, vinyl cyclohexene dioxide, 4-vinyl epoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 3,4-epoxy-6-methylcyclohexyl carboxylate, methylene bis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, ethylene glycol di(3,4-epoxycyclohexylmethyl) ether, ethylene bis(3,4-epoxycyclohexane carboxylate), dioctyl epoxyhexahydrophthalate, di-2-ethylhexyl epoxyhexahydrophthalate, and the like.

And also, examples of the aliphatic epoxy resins described above, include polyglycidyl ethers of aliphatic polyhydric alcohols or their alkylene oxide adducts, polyglycidyl esters of aliphatic, long chain, poly-basic acids, homopolymers of glycidyl acrylate or methacrylate prepared by vinyl polymerization, copolymers of glycidyl acrylate or methacrylate, prepared by vinyl polymerization with other vinyl monomer and the like. Typical examples of such compounds include glycidyl ethers of polyhydric alcohols, such as 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, triglycidyl ether of glycerol, triglycidyl ether of trimethylol propane, tetraglycidyl ether of sorbitol, hexaglycidyl ether of dipentaerythritol, diglycidyl ether of polyethylene glycol, and diglycidyl ether of polypropylene glycol; polyglycidyl ethers of polyether-polymers, which can be obtained by adding one or more alkylene oxides with aliphatic polyhydric alcohols such as propylene glycol, trimethylol propane and glycerol; and diglycidyl esters of aliphatic, long chain di-basic acids. Further, mention may be made of mono-glycidyl ethers of aliphatic higher alcohols; mono-glycidyl ethers of phenol, cresol, butyl phenol, or polyether alcohols which can be obtained by adding alkylene oxide thereto; glycidyl esters of higher fatty acids; epoxidized soybean oil; octyl epoxy-stearate; butyl epoxy-stearate; epoxidized linseed oil; epoxidized polybutadiene and the like.

Examples of cationically polymerizing organic compounds except for epoxy compounds, which can be employ in this invention, include trimethylene oxide, oxetane compounds such as 3,3-dimethyl oxetane and 3,3-dichloromethyl oxetane; trioxane such as tetrahydrofuran and 2,3-dimethyltetrahydrofuran; cyclic ether compounds such as 1,3-dioxane and 1,3,6-trioxa-cyclooctane; cyclic lactones such as β -propiolactone, γ -butyrolactone and ϵ -caprolactone; thiiran compounds such as ethylene sulfide; thietane compounds such as trimethylene sulfide and 3,3-dimethyl thietane; cyclic thio-ether compounds such as tetrahydro-thiophene derivatives; spiro-ortho ester compounds obtained by the reaction of epoxy compounds with lactones; vinyl ether compounds such as ethylene glycol divinyl ether, alkyl vinyl ether, 3,4-dihydropyran-2-methyl (3,4-dihydropyran-2-carboxylate) and triethylene glycol divinyl ether; ethylenic unsaturated compounds such as styrene, vinyl cyclohexene, iso-butylene and polybutadiene, and the derivatives thereof, spiro-ortho carbonate compounds, cyclo carbonate compounds.

According to the present invention, the content of the (3) cationically polymerizing organic substance except for that having the general formula (1) mentioned above is preferably not more than 500 parts by weight per 100 parts of the cationically polymerizing organic substance having the general formula (1) mentioned above.

The content of the (2) energy beam sensitive cationic polymerization initiator is 0.05 to 30 wt%, preferably 0.5 to 10 wt%, based on the (1) cationically polymerizing organic substance having the general formula (1) mentioned above, or the sum of the (1) cationically polymerizing organic substance having the aforementioned general formula (1) and the (3) cationically polymerizing organic substance except for that having the aforementioned general formula (1). If this content is less than 0.05 wt%, the sensitivity becomes inferior; on the other hand, if this content is more than 30 wt%, curing property and adhesion property become inferior, and the resulting cured article is apt to get coloring.

(4) Radically polymerizing organic compound, which is used according to the present invention, is a radically polymerizing organic compound which polymerizes or cross-links upon exposure to an energy beam in the presence of a energy beam sensitive radical polymerization initiator and, preferably, has at least one unsaturated double bond per one molecule.

Examples of such compounds include acrylate compounds, methacrylate compounds, allyl urethane compounds, unsaturated polyester compounds, and styrene series compounds.

Among these radically polymerizing organic compounds, those having (meth)acrylic groups, such as epoxy (meth)acrylates, urethane (meth)acrylates, polyester (meth)acrylates, polyether (meth)acrylates, (meth)acrylic esters of alcohols, are best suited, for their availability and ease of synthesis and handling.

Here, epoxy (meth)acrylates refer to acrylates which are obtained by the reaction of, for example, a known aromatic, alicyclic or aliphatic epoxy resin and (meth)acrylic acid. The most preferable of these epoxy acrylates are the acrylates of aromatic epoxy resins which are obtained by the reaction of a polyglycidyl ether of a polyhydric phenol having at least one aromatic nuclei or an added alkylene oxide thereof, and (meth)acrylic acid. One example is the (meth)acrylate obtained by the reaction of a glycidyl ether and (meth)acrylic acid, the former obtained by the reaction of bisphenol A or an added alkylene oxide thereof and epichlorohydrin. Another example is the (meth)acrylate obtained by the reaction of an epoxy novolac resin and (meth)acrylic acid.

The most preferable urethane (meth)acrylates are those obtained by the reaction of one or more polyesters or polyethers having a hydroxyl group, a (meth)acrylic ester having a hydroxyl group, and an isocyanate, and those obtained by the reaction of a (meth)acrylic ester having a hydroxyl group and an isocyanate.

Among polyesters having a hydroxyl group, the most preferable ones are those obtained by the reaction of one or more polyhydric alcohols and one or more polybasic acids or one or more lactones. Examples of the polyhydric alcohols include 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, polybutylene glycol, trimethylolpropane, glycerol, pentaerythritol, and dipentaerythritol.

Examples of the polybasic acids include adipic acid, terephthalic acid, phthalic anhydride, and trimellitic acid. Examples of the lactones include β -propiolactone, γ -butyrolactone and ϵ -caprolactone.

Among polyethers having a hydroxyl group, the most preferable ones are those obtained by adding one or more alkylene oxides to a polyhydric alcohol. Examples of the polyhydric alcohols are such as those listed above. Examples of the alkylene oxides include ethylene oxide propylene oxide and butylene oxide.

Among (meth)acrylic esters having a hydroxyl group, the most preferable ones are those obtained by the esterification of a polyhydric alcohol and (meth)acrylic acid. Examples of the polyhydric alcohols are such as those listed above.

The best suited of these (meth)acrylic esters having a hydroxyl group are those obtained by the esterification of a dihydric alcohol and (meth)acrylic acid, such as 2-hydroxyethyl (meth)acrylate.

Among isocyanates, the most preferable ones are those having at least one or more isocyanic group per one molecule, particularly divalent isocyanic compounds such as tolylene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate.

The most preferable polyester (meth)acrylates are those obtained by the reaction of a polyester having a hydroxyl group and (meth)acrylic acid. Among polyesters having a hydroxyl group, the most preferable ones are those obtained

by the esterification of one or more polyhydric alcohols and one or more monoacids, polybasic acids. Examples of the polyhydric alcohols are such as those listed above. Examples of the monoacids include formic acid, acetic acid, butyric acid, and benzoic acid. Examples of the polybasic acids include adipic acid, terephthalic acid, phthalic anhydride, and trimellitic acid.

5 The most preferable polyether (meth)acrylates are those obtained by the reaction of a polyether having a hydroxyl group and (meth)acrylic acid. Among polyethers having a hydroxyl group, the most preferable ones are those obtained by adding one or more alkylene oxides to a polyhydric alcohol. Examples of the polyhydric alcohols are such as those listed above. Examples of the alkylene oxides include ethylene oxide, propylene oxide and butylene oxide.

10 The most preferable (meth)acrylic esters of alcohols are (meth)acrylates obtained by the reaction of an aromatic or aliphatic alcohol having at least one hydroxyl group per one molecule or an added alkylene oxide thereof, and (meth)acrylic acid. Examples of such (meth)acrylates include 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, isoamyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isooctyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isobonyl (meth)acrylate, benzyl (meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol di(meth)acrylates, polypropylene glycol di(meth)acrylates, trimethylolpropane tri(meth)acrylate, ethylene oxide-modified trimethylolpropane tri(meth)acrylate, propylene oxide-modified trimethylolpropane tri(meth)acrylate, pentaerythritol tetra (meth)acrylate, dipentaerythritol hexa(meth)acrylate, and ϵ -caprolactone-modified dipentaerythritol hexa(meth)acrylate.

15 In this invention, it is also preferable that 50 parts by weight or more of the (4) radically polymerizing organic compound, per 100 parts by weight, is a compound having (meth)acrylic group in the molecule.

20 The content of the (4) radically polymerizing organic compound used in this invention is preferably not more than 200 parts by weight, particularly preferably not more than 100 parts by weight, per 100 parts by weight of the cationically polymerizing organic substances.

25 The (5) energy beam sensitive radical polymerization initiator, used in this invention, is a compound, which enables to initiate the radical polymerization upon exposure to an energy beam, and preferably includes ketone series compounds such as acetophenone series compounds, benzyl series compounds and thioxanthone series compounds.

30 Acetophenone series compounds include, for example, diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropane-1-one, 4¹-iso-propyl-2-hydroxy-2-methylpropiophenone, 2-hydroxymethyl-2-methylpropiophenone, 2,2-dimethoxy-1,2-diphenylethane-1-one, p-dimethylaminoacetophenone, p-tert-butylidichloroacetophenone, p-tert-butyltrichloroacetophenone, p-azidobenzalacetophenone, 1-hydroxycyclohexylphenylketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin-n-butyl ether, benzoin isobutyl ether and the like.

Benzyl series compounds include benzyl, anisyl and the like.

35 Benzophenone series compounds include, for example, benzophenone, methyl α -benzoyl benzoate, Michler's ketone, 4,4'-bisdiethylamino benzophenone, 4,4'-dichlorobenzophenone, 4-benzoyl-4'-methyl diphenyl sulfide and the like. Thioxanthone series compounds include thioxanthone, 2-methylthioxanthone, 2-ethylthioxanthone, 2-chlorothioxanthone, 2-isopropylthioxanthone, 2,4-diethylthioxanthone and the like.

40 Other energy beam sensitive radical polymerization initiators include 2,4,6-trimethylbenzoyldiphenyl phosphine oxide, bis(cyclopentadienyl)-bis[2,6-difluoro-3-(p-yl-1-yl)]titanium and the like.

45 The above (5) energy beam sensitive radical polymerization initiators maybe used independently or in combination to attain a desired property.

If desired, a photosensitizer, which is not essential, may be added in the energy beam curable epoxy resin composition of this invention in the range of this invention. The combination of the photo-sensitizer such as anthracene derivative or pyrene derivative further improves the cure rate compared with the resin composition without the photo-sensitizer, and as a result, more preferable energy beam curable epoxy resin can be obtained. Generally, the content of the photo-sensitizer is 20 to 300 wt% based on the (2) energy beam sensitive cation polymerization initiator.

50 Organic compounds having two or more hydroxyl groups per one molecule, which are not essential component, may be added in the energy beam curable epoxy resin composition according to the present invention in the range of this invention. When organic compounds having two or more hydroxyl groups per one molecule, such as polyhydric alcohols, polyethers containing hydroxy groups, polyesters containing hydroxy groups and polyhydric phenols are added in the resin composition, flexible cured articles can be obtained.

55 Examples of the polyhydric alcohols include ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and the like.

The polyether containing hydroxy groups means a compound obtained by adding one or more alkylene oxide to one or more polyhydric alcohols or one or more polyhydric phenols. Examples of the polyhydric alcohols used therein include ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, polyhydric phenols used therein include bisphenol A, bisphenol F, phenol novolak, cresol novolak and the like. On the other hands, examples of the alkylene oxides include butylen

oxide, propylene oxide, ethylene oxide and the like.

Further, the polyester containing hydroxy groups means a polyester obtained by esterification of one or more monobasic or polybasic acids and one or more polyhydric alcohols or polyhydric phenols, and a polyester obtained by esterification of one or more lactones and one or more polyhydric alcohols. Examples of the polyhydric alcohols or polyhydric phenols such as those listed above. Examples of the monobasic acids include formic acid, acetic acid, butyric acid, benzoic acid and the like. Examples of the polybasic acids include adipic acid, terephthalic acid, trimellitic acid and the like. Examples of the lactones include β -propiolactone, γ -butyrolactone and ϵ -caprolactone.

The polyhydric phenol means a compound containing two or more hydroxy groups, bonded directly to aromatic ring, per one molecule, such as those listed above.

10 The content of the organic compound having two or more hydroxy groups per one molecule is 1 to 5 wt% based on the (1) cationically polymerizing organic substance having the general formula (I) mentioned above, or the sum of the (1) cationically polymerizing organic substance having the general formula (I) mentioned above and the (3) cationically polymerizing organic substance except for that having the general formula (I) mentioned above.

15 Thermoplastic polymers, which are not essential, may be added in the energy beam curable epoxy resin composition according to the present invention in the range of this invention. The thermoplastic polymer compound is a polymer compound which is in a liquid or solid state at room temperature and can be uniformly mixed with the resin composition at room temperature.

20 Typical examples of such thermoplastic polymer compounds include polyester, polyvinyl acetate, polyvinyl chloride, polybutadiene, polycarbonate, polystyrene, polyvinyl ether, polyvinylbutyral, polyacrylate, polymethyl methacrylate, polybutene, and styrene-butadiene block copolymer hydrogenated. Derivatives of these thermoplastic polymer compounds having functional groups such as a hydroxyl, carboxyl, vinyl or epoxy group may also be used. The preferable number-average molecular weight of said thermoplastic polymer compound as used in the present invention is 1000 to 500000, most preferably 5000 to 100000.

25 The energy beam curable epoxy resin composition according to the present invention with the thermoplastic polymer compound further improves the mechanical properties of the cured resin, compared with the same composition without it, and as a result, the resulting composition is more preferable. The content of the thermoplastic polymer compound is generally 3 to 100 wt% based on the (1) cationically polymerizing organic substance having the general formula (I) mentioned above, or the sum of (1) and (3) cationically polymerizing organic substance except for (1), or the sum of (1), (3) and (4) radically polymerizing organic compound.

30 Further, fillers, which are not essential, may be added in the energy beam curable epoxy resin composition of this invention in the range of this invention. The fillers mean inorganic or organic, powdered, flaky or fibrous materials.

35 Examples of inorganic fillers include glass powder, mica powder, silica powder or powder of ground quartz, carbon powder, powder of calcium carbonate, almina powder, powder of aluminium hydroxide, powder of aluminium silicate, powder of zirconium silicate, powder of iron oxide, powder of barium sulfate, kaolin, dolomite, metal powder, glass fiber, carbon fiber, asbestos, metallic whisker, whiskering calcium carbonate, hollow glass balloon and products bound with organic groups on the surface thereof by treating with coupling agent.

40 Examples of organic fillers include pulp powder, nylon powder, polyethylene powder, powder of crosslinked polystyrene, powder of crosslinked acrylic resin, powder of crosslinked phenol resin, powder of crosslinked urea resin, powder of crosslinked melamine resin, powder of crosslinked epoxy resin, powdered rubber, and products bound with reactive groups such as epoxy group, acrylic group or hydroxyl group on the surface thereof. The content of fillers is generally 0.5 to 30 wt%, preferably 1 to 20 wt%, based on the (1) cationically polymerizing organic substance having the general formula (I) mentioned above, or the sum of (1) and (3) cationically polymerizing organic substance except for (1), or the sum of (1), (3) and (4) radically polymerizing organic compound.

45 Various resin additives, such as thermosensitive cationic polymerization initiator, coloring agent such as pigment or dye, leveling agent, defoamer, thickener, flame retardant, antioxidant and stabilizer may be added as desired in the amounts of their normal use, provided that they do not impair the advantage of the present invention.

As the thermosensitive cationic polymerization initiator, for example, onium salts such as 2-butyryl tetramethylene sulfonium hexafluoroantimonate and 3-methyl-2-butyryl tetramethylene sulfonium hexafluoroantimonate, described in Japanese Patent Application Laid-open No. SHO 57-49613 and SHO 58-37004, can be mentioned.

50 The active energy beam required to cure the energy beam curable epoxy resin composition according to the present invention may be an ultraviolet ray, an electron beam, an X-ray, a radioactive ray, or a high-frequency wave, preferably an ultraviolet ray for the economical reason. Examples of a source of the ultraviolet ray include an ultraviolet laser, a mercury lamp, a xenon lamp, a sodium lamp, and an alkali metal lamp.

55 The energy beam curing epoxy resin composition of the present invention can be applied to metal, rubber, plastic, molding article, film, paper, wood, glass, concrete, ceramic article, etc.

On the other hand, as the embodiment of application, the energy beam curing epoxy resin composition can be used for paint and varnish, coating, ink, resist, adhesive, molding compound, casting material, putty, impregnant, etc.

Then, the detail of the stereolithographic resin composition and the stereolithographic method is set forth as follows.

As the stereolithographic resin composition of the present invention, the energy beam curing epoxy resin composition of the present invention described above can be used as such.

To carry out the stereolithographic method of the present invention, it is necessary to previously prepare an energy beam curing epoxy resin composition to be used as a stereolithographic resin composition.

5 This preparing process may be performed in a known manner by, for example, thoroughly mixing the components by blade turbine agitation, roll kneading, or other method. The preferred compounding ratio of (1) and (2), (1), (2) and (3), or (1), (2), (3), (4) and (5), which are the essential components of the stereolithographic resin composition, and the types and contents of the additives to be mixed as necessary may be selected according to the aforementioned compounding ratio of the energy beam curing epoxy resin composition. Thus obtained stereolithographic resin composition is generally in a liquid state at room temperature.

10 In the next step, a given portion of the stereolithographic resin composition is exposed to an energy beam to cure the exposed portion thereof, in order to produce a desired thickness of cured layer; then, the cured layer is overlaid with another layer of the energy beam curing resin composition, which is radio-cured in the same manner to produce a cured layer which continuously overlaps the first above-described cured; and the same process is repeated to finally obtain a three-dimensional solid shape. For example, the resin composition is placed in a vessel such as one described in Japanese Patent Application Laid-open No.60-247515; a light guide is set on the surface of the resin composition; a selected portion of the surface of the resin composition is exposed to an active energy beam, which is necessary for curing, through the light guide, while moving the light guide relative to the vessel, to obtain a desired solid shape.

15 The type of the active energy beam required for the stereolithographic method according to the present invention is the same as the active energy beam used for curing the energy beam curable resin composition according to the present invention. That is, an ultraviolet ray, an electron beam, an X-ray, a radioactive ray, or a high-frequency wave may be used, preferably an ultraviolet ray for the economical reason. Examples of a source of an ultraviolet ray include an ultraviolet laser, a mercury lamp, a xenon lamp, a sodium lamp, and an alkali metal lamp. The most preferable source is a laser for its superior light convergence property.

20 25 The following examples and comparative examples are given for the purpose of illustration for the embodiment of this invention.

Examples 1 to 20, Comparative Examples 1 to 10

30 The energy beam curable resin compositions shown in Tables 1 and 2 were obtained by uniformly mixing components. Numerical values shown in Tables are "parts by weight".

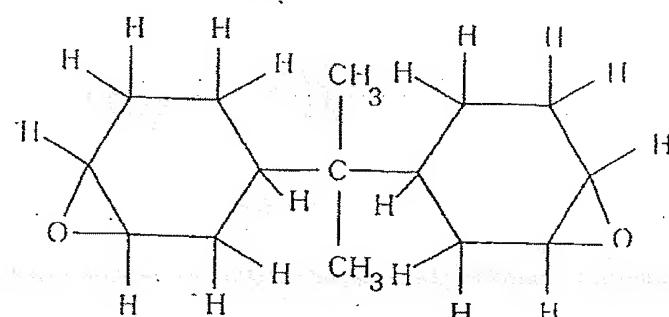
In Tables, epoxy resins as a cationically polymerizing organic substance and energy beam sensitive cation polymerization initiators, which were used in each Example and each Comparative Example, are expressed as follows:

35 Epoxy resin A : 2,2-bis(3,4-epoxy cyclohexyl) propane,

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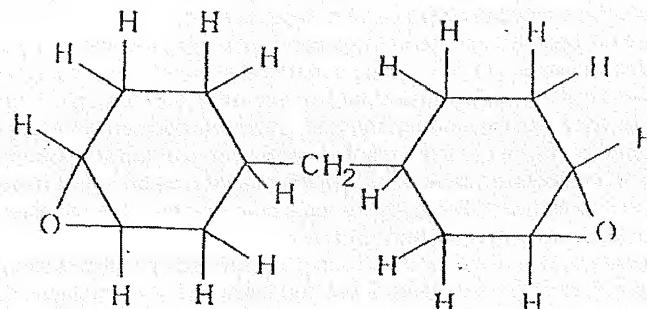
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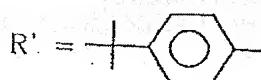
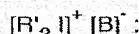
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Epoxy resin B : methylenebis(3,4-epoxy cyclohexane),

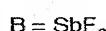
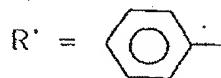
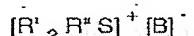


15 Epoxy resin C : 3,4-epoxy cyclohexylmethyl-3,4-epoxy cyclohexane carboxylate,
Epoxy resin D : bis(3,4-epoxy cyclohexylmethyl) adipate,
Epoxy resin E : 1,4-butanediol diglycidyl ether,

Initiator 1 : di-(4-tert-butylphenyl) iodonium hexafluorophosphate,

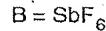
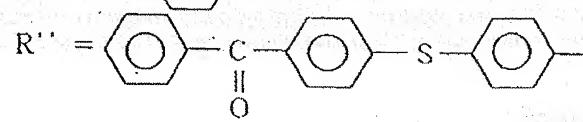


Initiator 2 : diphenyl-4-thiophenoxyphenyl sulfonium hexafluoroantimonate,

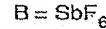
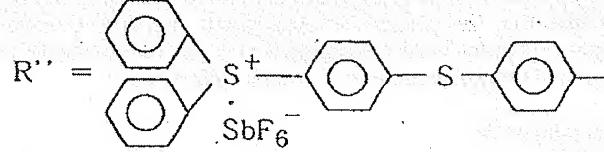
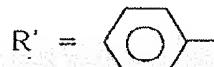
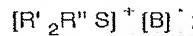


50 Initiator 3: 4-[4'-(benzoyl) phenylthio] phenyl-di-(4-fluorophenyl) sulfonium hexafluoroantimonate.

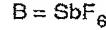
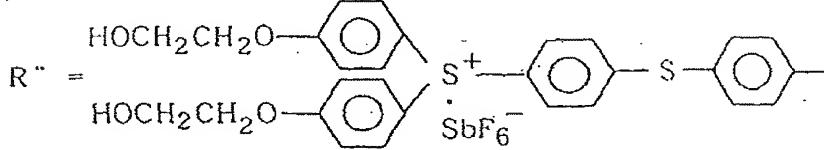
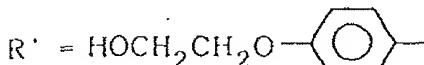
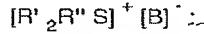




Initiator 4 : 4,4'-bis (diphenylsulfonio) phenylsulfid-bis-hexafluoroantimonate,



Initiator 5 : 4,4'-bis-[di(β -hydroxyethoxy) phenylsulfonio] phenylsulfid-bis-hexafluoroantimonate,



Here, the evaluations of the properties tested in Tables 1 and 2 were performed by the following methods.

[Degree of transparency]

Degree of transparency of the compositions was determined by visual evaluation.

O: completely transparent A: slightly turbid X: turbid

[Degree of dry tack]

The testing resin composition was coated on aluminum test panel with 5 μm of thickness, then the test panel was exposed to ultraviolet ray from the distance of 10 cm by a high-pressure mercury lamp (80 w/cm) to cure the coating surface, and the exposed dose (mJ/cm²) was determined until reaching to dry tack on the coating surface of the test panel.

O: less than 50 mJ/cm²

¹⁰ Δ: from 50 mJ/cm² to less than 100 mJ/cm²

X: equal to or more than 100 mJ/cm²

[Brightness]

The cured coating surface was determined by visual evaluation after the coating surface was exposed to ultraviolet ray until reaching to dry tack.

O: good brightness Δ: cloudy X: no brightness

[Alkali Resistant]

The resin composition to be tested was coated on a bonderized steel with 20 μm of thickness, then exposed with 100 mJ/cm² of dose by a high-pressure mercury-vapor lamp to form a cured coating film. A solution of 1N-NaOH was dropped on the cured coating film. The coating film was held horizontally to prevent removing of liquid and covered with a dish to prevent vaporizing of liquid. After keeping for 24 hrs., the coating film was washed by running water and then the change of the coating film was observed by visual evaluation.

²⁵ O: no change Δ: whitening of film

X: disappearance of film

[Water absorption]

The resin composition to be tested was injected into the space between two glass plates sandwiching a spacer with 3mm of thickness, and exposed to ultraviolet ray to produce a specimen (30mm x 30mm x 3mm). Ultraviolet ray was exposed with 2000 mJ/cm² dose by a high-pressure mercury-lamp (80 w/cm). Water absorption of the specimen was determined according to JIS-K6911.

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Table I

	Example					Comparative example									
	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5
Epoxy resin A	100	100	100	100	100				50	50					
Epoxy resin B						100	100	50	50						
Epoxy resin C										100	100	50	50		
Epoxy resin D												50	50		
Epoxy resin E															
Initiator 1		3									3				
Initiator 2		2													
Initiator 3		2				2						2			
Initiator 4			2				2		2				2	2	
Initiator 5				2				2			2				2
Transparency ¹	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Dry tack ²	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Brightness ³	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Alkali resist. ⁴	○	○	○	○	○	○	○	○	○	○	×	×	×	×	○
Water abs. (%) ⁵	0.29	0.29	0.28	0.26	0.25	0.3	0.31	0.32	0.37	0.35	1.01	0.98	0.97	0.91	0.92

Note

- 1 : degree of transparency
- 2 : degree of dry tack
- 3 : brightness
- 4 : alkali resistance
- 5 : water absorption (%)

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Table 2

	Example										Comparative example				
Epoxy resin A	11	12	13	14	15	16	17	18	19	20	6	7	8	9	10
Epoxy resin A	80	80	80	80					80	80					
Epoxy resin B					80	80	80								
Epoxy resin C									20		80	80	80	80	
Epoxy resin D										20					80
Epoxy resin E	20	20	20	20	20	20	20				20	20	20	20	20
Initiator 1	3										3				
Initiator 2	2														
Initiator 3		2													
Initiator 4			2									2			
Initiator 5				2									2		
Transparency	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Dry tack	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Brightness	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Alkali resist.	○	○	○	○	○	○	○	○	○	○	△	△	△	△	×
Water abs. (%)	0.36	0.3	0.31	0.32	0.32	0.38	0.37	0.37	0.35	0.35	0.85	0.82	0.82	0.82	0.92

Examples 21 to 28, Comparative Examples 11, 12

A stereolithographic molding was carried out as follows:

5 Example 21

According to the resin formulation (numerical value means "parts by weight") as shown in Table 3, a stereolithographic resin composition was obtained by thoroughly mixing the following:

10 (1) 50 parts by weight of the aforementioned Epoxy resin A and 50 parts by weight of the aforementioned Epoxy resin B as a cationically polymerizing organic substance, and
 (2) 3 parts by weight of the aforementioned Initiator 4 as an energy beam sensitive cationic polymerization initiator. The obtained resin composition was a transparent light-yellow liquid.

15 Then, a hollow and cylindrical test specimen, 9cm in height, 5cm in diameter, was obtained from the above resin composition by curing it in steps of 0.1 mm thickness according to CAD data, using a stereolithographic experiment system consisted of a three-dimensional numerically controlled table on which a container for the resin composition was to be placed, an ultraviolet argon laser (wavelength: 339, 351 and 364 nm multiline, output: 100mV), and a control unit comprising an optical system and a control computer. It took 70 minutes to obtain this specimen. The precision of the molding was 0.06% in height, and 0.03% in diameter relative to the design dimensions. Also, a hollow specimen "3mm x 10mm x 50mm" was prepared in order to test the change resulted from absorption of water. This specimen was dried holding in a decicator for five days. The specimen was held for 5 days in a thermo-hygrostat in which the temperature was 30 °C and the humidity was 90% RH, and then the coefficient of expansion "%" occurred by humidity was determined from 50mm of the length of the side. As the result, the coefficient of expansion was 0.01%.

25 Examples 22 to 28, Comparative Examples 11, 12

30 According to the resin formulation (numerical value means "parts by weight") as shown in Table 3, the each resin composition was prepared and tested in the same manner as in Example 21. The test results are shown in Table 3, together with the result of Example 21. Thus, the compounds used in these tests, except for the aforementioned compounds are shown as follows:

For the radically polymerizing organic compounds (hereafter "radical resin"), radical resins 1 through 3 as shown below were used:

35 Radical resin 1: bisphenol A diglycidyl ether diacrylate.
 Radical resin 2: trimethylolpropane triacrylate.
 Radical resin 3: dipentaerythritol hexaacrylate.

40 For energy beam sensitive radical polymerization initiators (hereafter "radical initiators"), radical initiators 1 and 2 as shown below were used:

45 Radical initiator 1: 1-hydroxy-cyclohexyl-phenyl ketone.
 Radical initiator 2: 2,2-dimethoxy-1,2-diphenylmethane-1-one.

Table 3

	Example								Comparative example	
	21	22	23	24	25	26	27	28	11	12
Epoxy resin A	50	20	50		40	70	40			
Epoxy resin B	50	80		70	20			60		
Epoxy resin C			40	20			20	10	70	60
Epoxy resin D			10						30	20
Epoxy resin E				10						
Initiator 3			2							2

Table 3 (continued)

	Example								Comparative example	
	21	22	23	24	25	26	27	28	11	12
5	Initiator 4	3			2	2				
10	Initiator 5		5				3	3	3	
15	Radical resin 1				20		20	30		20
20	Radical resin 2				20	20				
25	Radical resin 3					10	10			
30	Radical Initiator 1				2		3	2		2
35	Radical Initiator 2					2				
40	Molding time (min)	70	70	60	60	50	50	55	100	70
45	Precision (height, %)	0.06	0.05	0.06	0.06	0.09	0.1	0.08	0.06	0.1
50	Precision (rad,%) ⁶	0.03	0.03	0.04	0.03	0.02	0.05	0.04	0.02	0.03
55	Expansion by water (%) ⁷	0.01	0.02	0.01	0.02	0.01	0.02	0.04	0.03	0.6
60	Expansion by water absorption									0.45

Note

6 : Precision of radial direction

7 : Expansion by water absorption

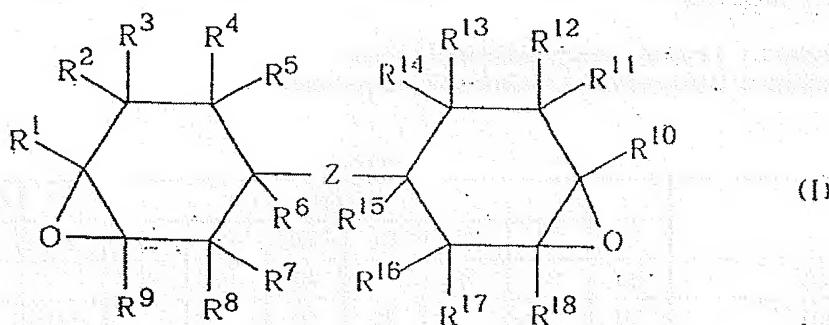
Industrial Feasibility

As described above, according to the present invention, an energy beam curable resin composition, the cured articles having such superior physical properties as improved chemical resistance, water-resistance, humidity resistance, adhesion property and reduced shrinkage on curing, as well as superior dimensional stability on humidity-absorption, can be obtained. And therefore, a stereolithographic resin composition and a stereolithographic method using the said resin composition can be also obtained.

Claims

1. An energy beam curing epoxy resin composition comprising, as essential components thereof:

(1) a cationically polymerizing organic substance having the general formula, as follows,



wherein 'Z' is a radical, having a valence of 2, selected from the group consisting of oxygen, sulfur, -NH-, -SO₂-, -CH₂-, -C(CH₃)₂-, -CBr₂-, C(CBr₃)₂ and -C(CF₃)₂, and R¹~R¹⁸, which may be identical or non-identical to each other, are hydrogen, halogen, hydrocarbon group, which may contain oxygen or halogen, or alkoxy group, which may be substituted; and

(2) an energy beam sensitive cationic polymerization initiator.

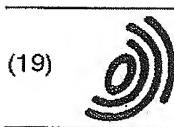
2. The energy beam curable epoxy resin composition according to Claim 1, which further comprises,
 - (3) a cationically polymerizing organic substance except for that of the aforementioned general formula (I).
- 5 3. The energy beam curable epoxy resin composition according to Claim 1 or 2, which further comprises,
 - (4) a radically polymerizing organic compounds; and
 - (5) an energy beam sensitive radical polymerization initiator.
- 10 4. The energy beam curable epoxy resin composition according to Claim 3, wherein 50 wt% or more of the (4) radically polymerizing organic compound is a compound having (meth)acrylic group per one molecule.
- 15 5. The energy beam curing epoxy resin composition according to claims 3 or 4 wherein the radically polymerising organic compound (4) is selected from the group consisting of acrylate compounds, methacrylate compounds, allyl urethane compounds, unsaturated polyester compounds, and styrene series compounds.
- 20 6. The energy beam curing epoxy resin composition according to any of claims 3 to 5, wherein the energy beam sensitive radical polymerisation initiator (5) is selected from the group consisting of ketone series compounds such as acetophenone series compounds, benzyl series compounds and thioxanthone series compounds.
- 25 7. The energy beam curing epoxy resin composition according to any preceding claim wherein the energy beam sensitive cationic polymerisation initiator is selected from the group consisting of aromatic diazonium salts, aromatic iodonium salts, aromatic sulphonium salts, iron arene complexes, and aluminium complexes or mixtures thereof.
- 30 8. The energy beam curable epoxy resin composition according to claim 2 wherein the cationically polymerising organic substance (3), except for that the aforementioned general formula (I), is selected from the group consisting of epoxy compounds, cyclic ether compounds, cyclic lactone compounds, cyclic acetyl compounds, cyclic thioether compounds, spiroorthoester compounds, and vinyl compounds, all of which may be used independently or in combination.
- 35 9. A stereolithographic method, wherein a given portion of an energy beam curing resin composition is exposed to an energy beam to cure the exposed portion thereof, in order to produce a desired thickness of cured layer; then, the cured layer is overlaid with another layer of the energy beam curable resin composition, which is then cured in the same manner to produce a cured layer which continuously overlaps the first layer; and the same process is repeated to finally obtain a three-dimensional molding; which comprises using the resin composition of any preceding Claim.

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(22) Date of filing: 26.11.1997

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AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

Designated Extension States:
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(30) Priority: 26.11.1996 JP 31504796

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- Tachikawa, Hiroyuki
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- Ohkawa, Kazuo
7-chome, Arakawa-Ku, Tokyo 116 (JP)
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Gill Jennings & Every,
Broadgate House,
7 Eldon Street
London EC2M 7LH (GB)

(54) **Energy beam curable epoxy resin composition, stereolithographic resin composition and stereolithographic method**

(57) The energy beam curable epoxy resin composition comprising as essential components, (1) specific cationically polymerizing organic substance, (2) energy beam sensitive cation polymerization initiator, (3) cationically polymerizing organic substance except for the specific cationically polymerizing organic substance, described above, (4) radically polymerizing organic

compound, and (5) energy beam sensitive radical polymerization initiator. The cured articles resulted from said resin composition, have superior properties and particularly superior dimensional stability on humidity absorption. Therefore, a stereolithographic resin composition and a stereolithographic method are also provided.

EP 0 844 262 A3

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 9546

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 605 361 A (CIBA GEIGY AG) 6 July 1994 (1994-07-06) * page 4, line 22,23; claims 1,18,20 * ---	1-9	C08G59/68 C08G59/24 C08G59/30 C08L63/00 G03F7/038
A	US 4 260 465 A (VIA FRANCIS A) 7 April 1981 (1981-04-07) * column 2, line 33 - column 3, line 28 *	1-9	
A	EP 0 715 212 A (TEIJIN SEIKI CO LTD) 5 June 1996 (1996-06-05) * page 7, line 7-10; claim 7 *	1-9	
X	US 5 434 196 A (OHKAWA KAZUO ET AL) 18 July 1995 (1995-07-18) column 13, lines 60-67 * column 3, line 17-19; claim 1 *	1-9	
X	EP 0 360 869 A (ASAHI DENKA KOGYO KABUSHIKI KAISHA) 4 April 1990 (1990-04-04) * page 29, line 11-14; claim 3 *	1-8	
X	WO 96 35756 A (CHIKAOKA SATOYUKI ;OHKAWA KAZUO (JP); ASAHI DENKA KOGYO KK (JP)) 14 November 1996 (1996-11-14) (see corresponding passages in EP-A-0 831 127)	1-9	C08G C08L G03F
E	EP 0 831 127 A (ASAHI DENKA KOGYO KK) 25 March 1998 (1998-03-25) * page 3, line 54; claims 1-3,12 *	1-9	
X,P	WO 97 38354 A (DSM NV ;JAPAN SYNTHETIC RUBBER CO LTD (JP); JAPAN FINE COATINGS CO) 16 October 1997 (1997-10-16) * page 6, line 1-4; claims 1-8 *	1-9 -/-	

- The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	29 August 2000	Rousseau, F
CATEGORY OF CITED DOCUMENTS		
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		
T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons S: member of the same patent family, corresponding document		



CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
1-9 wherein Z is oxygen, sulfur, -CH₂- or -C(CH₃)₂-

None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 9546

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
E	EP 0 831 373 A (JAPAN SYNTHETIC RUBBER CO LTD ; JAPAN FINE COATINGS CO LTD (JP); DS) 25 March 1998 (1998-03-25) * page 3, line 35-42; claims 1-20 *	1-9	
X, P	WO 97 11122 A (MINNESOTA MINING & MFG ; YLITALO DAVID A (US); PEREZ MARIO A (US);) 27 March 1997 (1997-03-27) page 9, lines 19-22 * page 8, line 18-29; claims 1,8 *	1	
X	PATENT ABSTRACTS OF JAPAN vol. 014; no. 539 (C-0782), 28 November 1990 (1990-11-28) & JP 02 225580 A (RICOH CO LTD), 7 September 1990 (1990-09-07) page 3, formula (4) * abstract *	1,8	
Y	US 4 189 548 A (TAKESHI SAKASHITA ET AL) 19 February 1980 (1980-02-19) * column 18, line 45 *	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Y, D	EP 0 090 239 A (BAYER AG) 5 October 1983 (1983-10-05) * the whole document *	1-9	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	29 August 2000	Rousseau, F	
CATEGORY OF CITED DOCUMENTS			
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1. Claims: 1-9 (partially)

Subject-matters for which Z is oxygen.

2. Claims: 1-9 (partially)

Subject-matters for which Z is sulfur.

3. Claims: 1-9 (partially)

Subject-matters for which Z is -NH-.

4. Claims: 1-9 (partially)

Subject-matters for which Z is -SO-.

5. Claims: 1-9 (partially)

Subject-matters for which Z is -SO2-.

6. Claims: 1-9 (partially)

Subject-matters for which Z is -CH2-.

7. Claims: 1-9 (partially)

Subject-matters for which Z is -C(CH₃)₂-.

8. Claims: 1-9 (partially)

Subject-matters corresponding to Z = -CBr₂-.

9. Claims: 1-9 (partially)

Subject-matters corresponding to Z = -C(CBr₃)₂-.

10. Claims: 1-9 (partially)

Subject-matters corresponding to Z = -C(CF₃)₂-.

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 97 30 9546

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-08-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0605361 A	06-07-1994	AT 151085 T AU 658780 B AU 5252493 A CA 2111718 A DE 59306034 D ES 2100513 T JP 6228413 A US 5476748 A	15-04-1997 27-04-1995 30-06-1994 22-06-1994 07-05-1997 16-06-1997 16-08-1994 19-12-1995
US 4260465 A	07-04-1981	NONE	
EP 0715212 A	05-06-1996	JP 8224790 A US 5849459 A	03-09-1996 15-12-1998
US 5434196 A	18-07-1995	JP 1213304 A JP 8026121 B JP 2028261 A JP 2590215 B JP 2080422 A JP 2604438 B JP 2080423 A JP 2538652 B US 5525645 A AT 161860 T DE 68928521 D DE 68928521 T EP 0360869 A WO 8907620 A	28-08-1989 13-03-1996 30-01-1990 12-03-1997 20-03-1990 30-04-1997 20-03-1990 25-09-1996 11-06-1996 15-01-1998 12-02-1998 16-04-1998 04-04-1990 24-08-1989
EP 0360869 A	04-04-1990	JP 1213304 A JP 8026121 B JP 2028261 A JP 2590215 B JP 2080422 A JP 2604438 B JP 2080423 A JP 2538652 B DE 68928521 D DE 68928521 T AT 161860 T WO 8907620 A US 5434196 A US 5525645 A	28-08-1989 13-03-1996 30-01-1990 12-03-1997 20-03-1990 30-04-1997 20-03-1990 25-09-1996 12-02-1998 16-04-1998 15-01-1998 24-08-1989 18-07-1995 11-06-1996
WO 9635756 A	14-11-1996	EP 0831127 A	25-03-1998

EPO FORM P0559

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 97 30 9546

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29-08-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0831127	A	25-03-1998	WO 9635756 A	14-11-1996
WO 9738354	A	16-10-1997	JP 9278811 A AU 2309397 A EP 0892941 A	28-10-1997 29-10-1997 27-01-1999
EP 0831373	A	25-03-1998	JP 10087810 A	07-04-1998
WO 9711122	A	27-03-1997	AU 3679495 A BR 9510644 A EP 0851894 A JP 11513416 T	09-04-1997 05-01-1999 08-07-1998 16-11-1999
JP 02225580	A	07-09-1990	NONE	
US 4189548	A	19-02-1980	JP 54043259 A CA 1104293 A DE 2818333 A FR 2388830 A GB 1588299 A IT 1158694 B NL 7804500 A	05-04-1979 30-06-1981 09-11-1978 24-11-1978 23-04-1981 25-02-1987 30-10-1978
EP 0090239	A	05-10-1983	DE 3211305 A DE 3361824 D JP 58172387 A	29-09-1983 27-02-1986 11-10-1983

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

EPO FORM P0459

③ EPS1986
EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 2003013001
PUBLICATION DATE : 15-01-03

APPLICATION DATE : 26-06-01
APPLICATION NUMBER : 2001193430

APPLICANT : DAICEL CHEM IND LTD;

INVENTOR : TAKAI HIDEYUKI;

INT.CL. : C09D163/00 C09D 5/00 C09D157/10 C09D201/00

TITLE : ULTRAVIOLET LIGHT-CURING TYPE COATING MATERIAL COMPOSITION FOR CAN
AND METHOD FOR PRODUCING COATED METAL CAN

ABSTRACT : PROBLEM TO BE SOLVED: To provide an ultraviolet light-curing type coating material, capable of being cured by a low dose ultraviolet light irradiation, excellent in coated film performance such as processability, close adhesion, hardness and scratch- resistance, etc., especially capable of forming a coated film excellent in coated film appearance and retort resistance, and a coated metal can by using the above composition.

SOLUTION: This ultraviolet-light curing type coating material composition contains 10-100 pts.wt. of (A) a compound having an alicyclic epoxy group in the molecule and not having an ester bond, 0-90 pts.wt. of (B) a compound having an alicyclic epoxy group in the molecule and an ester group and/or epoxy compound having glycidyl group, 1-50 pts.wt. of a copolymer having glycidyl group and/or at least one alicyclic epoxy group in the molecule, and 0.01-20 pts.wt. of a cationic polymerization initiator each based on 100 pts.wt. total amount of the compounds (A) and (B).

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ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 97 30 9546

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-08-2000

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0831127	A	25-03-1998	WO	9635756 A		14-11-1996
WO 9738354	A	16-10-1997	JP	9278811 A		28-10-1997
			AU	2309397 A		29-10-1997
			EP	0892941 A		27-01-1999
EP 0831373	A	25-03-1998	JP	10087810 A		07-04-1998
WO 9711122	A	27-03-1997	AU	3679495 A		09-04-1997
			BR	9510644 A		05-01-1999
			EP	0851894 A		08-07-1998
			JP	11513416 T		16-11-1999
JP 02225580	A	07-09-1990		NONE		
US 4189548	A	19-02-1980	JP	54043259 A		05-04-1979
			CA	1104293 A		30-06-1981
			DE	2818333 A		09-11-1978
			FR	2388830 A		24-11-1978
			GB	1588299 A		23-04-1981
			IT	1158694 B		25-02-1987
			NL	7804500 A		30-10-1978
EP 0090239	A	05-10-1983	DE	3211305 A		29-09-1983
			DE	3361824 D		27-02-1986
			JP	58172387 A		11-10-1983

EPO FORM P049

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT
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US 4260465	A	07-04-1981	NONE	
EP 0715212	A	05-06-1996	JP 8224790 A US 5849459 A	03-09-1996 15-12-1998
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EP 0360869	A	04-04-1990	JP 1213304 A JP 8026121 B JP 2028261 A JP 2590215 B JP 2080422 A JP 2604438 B JP 2080423 A JP 2538652 B DE 68928521 D DE 68928521 T AT 161860 T WO 8907620 A US 5434196 A US 5525645 A	28-08-1989 13-03-1996 30-01-1990 12-03-1997 20-03-1990 30-04-1997 20-03-1990 25-09-1996 12-02-1998 16-04-1998 15-01-1998 24-08-1989 18-07-1995 11-06-1996
WO 9635756	A	14-11-1996	EP 0831127 A	25-03-1998

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



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2. Claims: 1-9 (partially)

Subject-matters for which Z is sulfur.

3. Claims: 1-9 (partially)

Subject-matters for which Z is $-\text{NH}-$.

4. Claims: 1-9 (partially)

Subject-matters for which Z is $-\text{SO}-$.

5. Claims: 1-9 (partially)

Subject-matters for which Z is $-\text{SO}_2-$.

6. Claims: 1-9 (partially)

Subject-matters for which Z is $-\text{CH}_2-$.

7. Claims: 1-9 (partially)

Subject-matters for which Z is $-\text{C}(\text{CH}_3)_2-$.

8. Claims: 1-9 (partially)

Subject-matters corresponding to Z = $-\text{CBr}_2-$.

9. Claims: 1-9 (partially)

Subject-matters corresponding to Z = $-\text{C}(\text{CBr}_3)_2-$.

10. Claims: 1-9 (partially)

Subject-matters corresponding to Z = $-\text{C}(\text{CF}_3)_2-$.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)		
E	EP 0 831 373 A (JAPAN SYNTHETIC RUBBER CO LTD ; JAPAN FINE COATINGS CO LTD (JP); DS) 25 March 1998 (1998-03-25) * page 3, line 35-42; claims 1-20 *	1-9			
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Place of search	Date of completion of the search	Examiner			
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CATEGORY OF CITED DOCUMENTS					
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P : intermediate document	& : member of the same patent family, corresponding document				

**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing more than ten claims.

Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
1-9 wherein Z is oxygen, sulfur, -CH₂- or -C(CH₃)₂-

None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



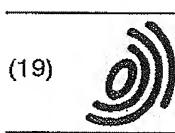
European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 97 30 9546

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(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 844 262 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
25.10.2000 Bulletin 2000/43

(51) Int Cl.7: C08G 59/68, C08G 59/24,
C08G 59/30, C08L 63/00,
G03F 7/038

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27.05.1998 Bulletin 1998/22

(21) Application number: 97309546.6

(22) Date of filing: 26.11.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 26.11.1996 JP 31504796

(71) Applicant: ASAHI DENKA KOGYO KABUSHIKI
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(72) Inventors:

• Akutsu, Mitsuo
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• Tachikawa, Hiroyuki
7-chome, Arakawa-Ku, Tokyo 116 (JP)
• Ohkawa, Kazuo
7-chome, Arakawa-Ku, Tokyo 116 (JP)
• Chikaoka, Satoyuki
7-chome, Arakawa-Ku, Tokyo 116 (JP)

(74) Representative: Jones, Helen Marjorie Meredith
Gill Jennings & Every,
Broadgate House,
7 Eldon Street
London EC2M 7LH (GB)

(54) Energy beam curable epoxy resin composition, stereolithographic resin composition and stereolithographic method

(57) The energy beam curable epoxy resin composition comprising as essential components, (1) specific cationically polymerizing organic substance, (2) energybeam sensitive cation polimerization initiator, (3) cationically polymerizing organic substance except for the specific cationically polymerizing organic substance, described above, (4) radically polymerizing organic

compound, and (5) energy beam sensitive radical polymerization initiator. The cured articles resulted from said resin composition, have superior properties and particularly superior dimensional stability on humidity absorption. Therefore, a stereolithographic resin composition and a stereolithographic method are also provided.

EP 0 844 262 A3

2. The energy beam curable epoxy resin composition according to Claim 1, which further comprises,
 (3) a cationically polymerizing organic substance except for that of the aforementioned general formula (I).

5 3. The energy beam curable epoxy resin composition according to Claim 1 or 2, which further comprises,
 (4) a radically polymerizing organic compounds; and
 (5) an energy beam sensitive radical polymerization initiator.

10 4. The energy beam curable epoxy resin composition according to Claim 3, wherein 50 wt% or more of the (4) radically polymerizing organic compound is a compound having (meth)acrylic group per one molecule.

15 5. The energy beam curing epoxy resin composition according to claims 3 or 4 wherein the radically polymerising organic compound (4) is selected from the group consisting of acrylate compounds, methacrylate compounds, allyl urethane compounds, unsaturated polyester compounds, and styrene series compounds.

20 6. The energy beam curing epoxy resin composition according to any of claims 3 to 5, wherein the energy beam sensitive radical polymerisation initiator (5) is selected from the group consisting of ketone series compounds such as acetophenone series compounds, benzyl series compounds and thioxanthone series compounds.

25 7. The energy beam curing epoxy resin composition according to any preceding claim wherein the energy beam sensitive cationic polymerisation initiator is selected from the group consisting of aromatic diazonium salts, aromatic iodonium salts, aromatic sulphonium salts, iron arene complexes, and aluminium complexes or mixtures thereof.

30 8. The energy beam curable epoxy resin composition according to claim 2 wherein the cationically polymerising organic substance (3), except for that the aforementioned general formula (I), is selected from the group consisting of epoxy compounds, cyclic ether compounds, cyclic lactone compounds, cyclic acetyl compounds, cyclic thioether compounds, spiroorthoester compounds, and vinyl compounds, all of which may be used independently or in combination.

35 9. A stereolithographic method, wherein a given portion of an energy beam curing resin composition is exposed to an energy beam to cure the exposed portion thereof, in order to produce a desired thickness of cured layer; then, the cured layer is overlaid with another layer of the energy beam curable resin composition, which is then cured in the same manner to produce a cured layer which continuously overlaps the first layer; and the same process is repeated to finally obtain a three-dimensional molding; which comprises using the resin composition of any preceding Claim.

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Table 3 (continued)

	Example								Comparative example	
	21	22	23	24	25	26	27	28	11	12
5	Initiator 4	8			2	2				
10	Initiator 5		5				3	3	3	
15	Radical resin 1					20		20	30	20
20	Radical resin 2					20	20			
	Radical resin 3						10	10		
	Radical Initiator 1					2		3	2	2
	Radical Initiator 2						2			
	Molding time (min)	70	70	60	60	50	50	55	55	100
	Precision (height, %)	0.06	0.05	0.06	0.06	0.09	0.1	0.08	0.06	0.06
	Precision (rad, %) ⁶	0.03	0.03	0.04	0.03	0.02	0.05	0.04	0.02	0.03
	Expansion by water (%) ⁷	0.01	0.02	0.01	0.02	0.01	0.02	0.04	0.03	0.6
	Expansion by water (%) ⁷	0.01	0.02	0.01	0.02	0.01	0.02	0.04	0.03	0.45

Note

6 : Precision of radial direction

7 : Expansion by water absorption

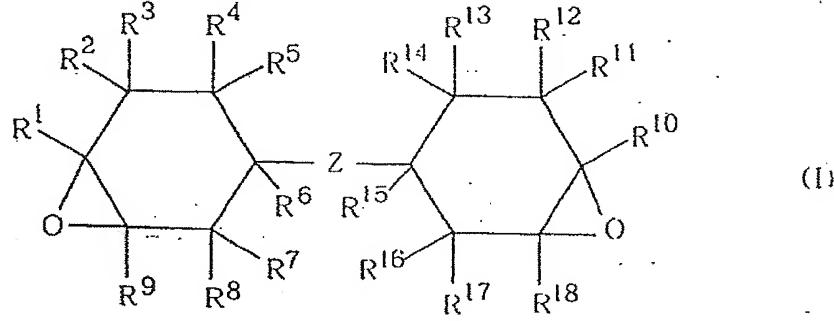
25 Industrial Feasibility

As described above, according to the present invention, an energy beam curable resin composition, the cured articles having such superior physical properties as improved chemical resistance, water-resistance, humidity resistance, adhesion property and reduced shrinkage on curing, as well as superior dimensional stability on humidity-absorption, can be obtained. And therefore, a stereolithographic resin composition and a stereolithographic method using the said resin composition can be also obtained.

35 Claims

1. An energy beam curing epoxy resin composition comprising, as essential components thereof:

(1) a cationically polymerizing organic substance having the general formula, as follows,



55 wherein 'Z' is a radical, having a valence of 2, selected from the group consisting of oxygen, sulfur, -NH-, -SO-, -SO₂-, -CH₂-, -C(CH₃)₂-, -CBr₂-, C(CBr₃)₂-, and -C(CF₃)₂-, and R¹~R¹⁸, which may be identical or non-identical to each other, are hydrogen, halogen, hydrocarbon group, which may contain oxygen or halogen, or alkoxy group, which may be substituted; and

(2) an energy beam sensitive cationic polymerization initiator.

Examples 21 to 28, Comparative Examples 11, 12

A stereolithographic molding was carried out as follows:

5 Example 21

According to the resin formulation (numerical value means "parts by weight") as shown in Table 3, a stereolithographic resin composition was obtained by thoroughly mixing the following:

10 (1) 50 parts by weight of the aforementioned Epoxy resin A and 50 parts by weight of the aforementioned Epoxy resin B as a cationically polymerizing organic substance, and
 (2) 3 parts by weight of the aforementioned Initiator 4 as an energy beam sensitive cationic polymerization initiator. The obtained resin composition was a transparent light-yellow liquid.

15 Then, a hollow and cylindrical test specimen, 9cm in height, 5cm in diameter, was obtained from the above resin composition by curing it in steps of 0.1 mm thickness according to CAD data, using a stereolithographic experiment system consisted of a three-dimensional numerically controlled table on which a container for the resin composition was to be placed, an ultraviolet argon laser (wavelength: 333, 351 and 364 nm multiline, output: 100mV), and a control unit comprising an optical system and a control computer. It took 70 minutes to obtain this specimen. The precision of the molding was 0.06% in height, and 0.03% in diameter relative to the design dimensions. Also, a hollow specimen "3mm x 10mm x 50mm" was prepared in order to test the change resulted from absorption of water. This specimen was dried holding in a decicator for five days. The specimen was held for 5 days in a thermo-hygrostat in which the temperature was 30 °C and the humidity was 90% RH, and then the coefficient of expansion "%" occurred by humidity was determined from 50mm of the length of the side. As the result, the coefficient of expansion was 0.01%.

25 Examples 22 to 28, Comparative Examples 11, 12

30 According to the resin formulation (numerical value means "parts by weight") as shown in Table 3, the each resin composition was prepared and tested in the same manner as in Example 21. The test results are shown in Table 3, together with the result of Example 21. Thus, the compounds used in these tests, except for the aforementioned compounds are shown as follows:

35 For the radically polymerizing organic compounds (hereafter "radical resin"), radical resins 1 through 3 as shown below were used:

35 Radical resin 1: bisphenol A diglycidyl ether diacrylate.
 Radical resin 2: trimethylolpropane triacrylate.
 Radical resin 3: dipentaerythritol hexaacrylate.

40 For energy beam sensitive radical polymerization initiators (hereafter "radical initiators"), radical initiators 1 and 2 as shown below were used:

45 Radical initiator 1: 1-hydroxy-cyclohexyl-phenyl ketone.
 Radical initiator 2: 2,2-dimethoxy-1,2-diphenylmethane-1-one.

Table 3

	Example								Comparative example	
	21	22	23	24	25	26	27	28	11	12
Epoxy resin A	50	20	50		40	70	40			
Epoxy resin B	50	80		70	20			60		
Epoxy resin C			40	20			20	10	70	60
Epoxy resin D			10						30	20
Epoxy resin E				10						
Initiator 3			2							2

Table 2

	Example										Comparative example				
	11	12	13	14	15	16	17	18	19	20	6	7	8	9	10
Epoxy resin A	80	80	80	80	80				80	80					
Epoxy resin B						80	80								
Epoxy resin C									20		80	80	80		
Epoxy resin D										20					80
Epoxy resin E	20	20	20	20	20	20	20	20			20	20	20	20	20
Initiator 1	3										3				
Initiator 2	2														
Initiator 3		2													
Initiator 4			2				2								
Initiator 5				2				2							
Transparency	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Dry tack	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Brightness	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Alkali resist.	○	○	○	○	○	○	○	○	○	○	△	△	△	△	×
Water abs. (%)	0.36	0.31	0.32	0.32	0.38	0.37	0.37	0.35	0.35	0.85	0.82	0.82	0.82	0.92	

Table I

	Example					Comparative example									
	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5
Epoxy resin A	100	100	100	100	100						50	50			
Epoxy resin B						100	100	100	50	50					
Epoxy resin C											100	100	50	50	50
Epoxy resin D													50	50	50
Epoxy resin E															
Initiator 1	3										3				
Initiator 2	2														
Initiator 3		2				2						2			
Initiator 4			2				2						2		
Initiator 5				2				2					2		2
Transparency ¹	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Dry tack ²	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Brightness ³	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Alkali resist. ⁴	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Water abs. (%) ⁵	0.29	0.29	0.28	0.26	0.25	0.3	0.31	0.32	0.37	0.35	1.01	0.98	0.97	0.91	0.92

Note

1 : degree of transparency

2 : degree of dry tack

3 : brightness

4 : alkali resistance

5 : water absorption (%)

[Degree of dry tack]

5 The testing resin composition was coated on aluminum test panel with 5 μm of thickness, then the test panel was exposed to ultraviolet ray from the distance of 10 cm by a high-pressure mercury lamp (80 w/cm) to cure the coating surface, and the exposed dose (mJ/cm²) was determined until reaching to dry tack on the coating surface of the test panel.

10 O: less than 50 mJ/cm²
Δ: from 50 mJ/cm² to less than 100 mJ/cm²
X: equal to or more than 100 mJ/cm²

[Brightness]

15 The cured coating surface was determined by visual evaluation after the coating surface was exposed to ultraviolet ray until reaching to dry tack.

O: good brightness Δ: cloudy X: no brightness

[Alkali Resistant]

20 The resin composition to be tested was coated on a bonderized steel with 20 μm of thickness, then exposed with 100 mJ/cm² of dose by a high-pressure mercury-vapor lamp to form a cured coating film. A solution of 1N-NaOH was dropped on the cured coating film. The coating film was held horizontally to prevent removing of liquid and covered with a dish to prevent vaporizing of liquid. After keeping for 24 hrs., the coating film was washed by running water and then the change of the coating film was observed by visual evaluation.

25 O: no change Δ: whitening of film
X: disappearance of film

[Water absorption]

30 The resin composition to be tested was injected into the space between two glass plates sandwiching a spacer with 3mm of thickness, and exposed to ultraviolet ray to produce a specimen (30mm x 30mm x 3mm). Ultraviolet ray was exposed with 2000 mJ/cm² dose by a high-pressure mercury-lamp (80 w/cm). Water absorption of the specimen was determined according to JIS-K6911.

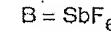
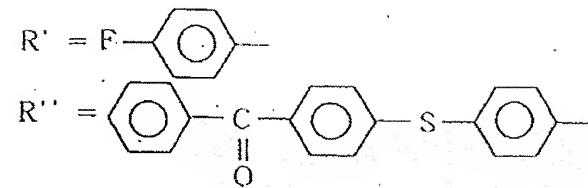
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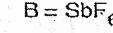
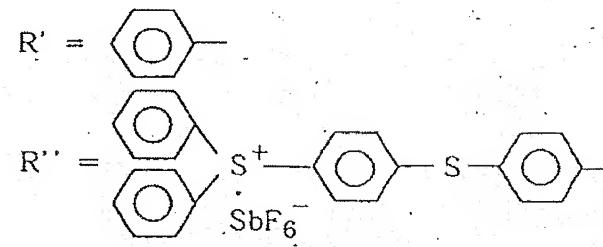
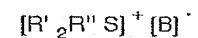
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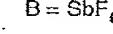
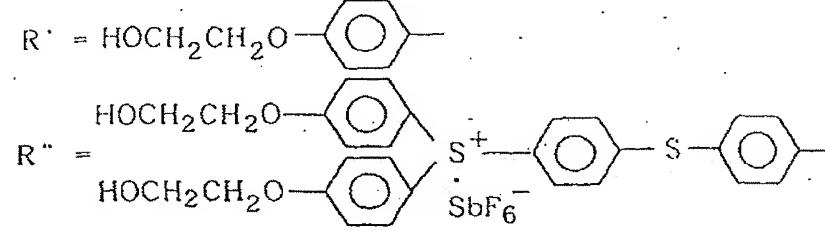
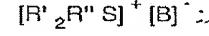
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Initiator 4 : 4,4'-bis (diphenylsulfonio) phenylsulfid-bis-hexafluoroantimonate,



Initiator 5 : 4,4'-bis-[di(β -hydroxyethoxy) phenylsulfonio] phenylsulfid-bis-hexafluoroantimonate,



Here, the evaluations of the properties tested in Tables 1 and 2 were performed by the following methods.

[Degree of transparency]

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Degree of transparency of the compositions was determined by visual evaluation.
 O: completely transparent A: slightly turbid X: turbid